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(21) International Application Number: PCT/US88/00415 (22) International Filing Date: 16 February 1988 (16.02.88) (31) Priority Application Number: 021,284 (32) Priority Date: 3 March 1987 (03.03.87) (33) Priority Country: US (71) Applicant: GAF CORPORATION [US/US]; 1361 Alps Road, Wayne, NJ 07470 (US). (72) Inventors: TRACY, David, J. ; 209 Comly Road, Lincoln Park, NJ 07035 (US). HASHEM, Mohamed, M. ; 100 Magnolia Place, Wayne, NJ 07470 (US). LOGIN, Robert, B. ; 137 Page Drive, Oakland, NJ 07436 (US). (74) Agents: MAUE, Marilyn, J. et al.; GAF Corporation, 1361 Alps Road, Wayne, NJ 07470 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report.</i>
(54) Title: POLYMERIC HALOPHORS (57) Abstract A stable iodine complex formed from the association of iodine with a pyrrolidonyl surfactant and its use in therapeutic, environmental and industrial applications and particularly as low foaming disinfectants for gradual release of iodine over significantly extended periods.		

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POLYMERIC HALOPHORS

Iodine complexes with methyl pyrrolidone for germicidal and disinfectant applications has long been known. However, the iodine disinfectant properties of this complex is dissipated in a relatively short period so that reapplication of the disinfectant treatment is required for protection over long periods. Also, for certain applications, e.g.. washing of contaminated equipment, hospital surroundings and animal disinfection, cleaning as well as germicidal, virucidal and sporicidal properties are required. Iodine/polyvinyl pyrrolidone complexes, which present numerous complexing sites in the molecule, have been developed for this purpose and, while these polymeric complexes, do in fact, extend the effective release of iodine over longer periods, they, like the methyl pyrrolidone/iodine complexes, lack the desired surfactant and detergent properties. Therefore, it is an aim of research to develop a disinfectant or germicide having extended iodine release time as well as non-foaming surfactant and cleaning properties so that such treatment need not be frequently repeated and removal of other soil or debris can be accomplished in a single washing treatment.

Accordingly it is an object of this invention to accomplish the above sought for needs.

Another object of this invention is to provide the release of iodine over an extended period of time by a method which is commercially feasible and economical.

Another object is to provide a low foaming surfactant which inherently possesses disinfectant properties.

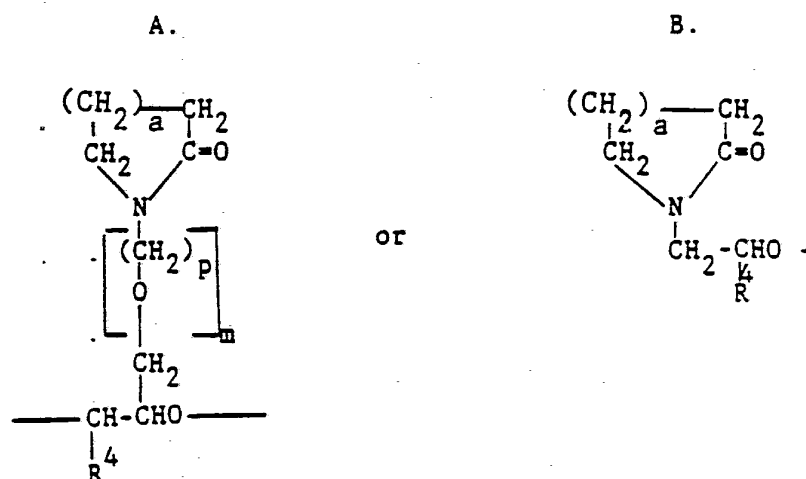
These and other objects of the invention will become apparent from the following description and disclosure.

SUBSTITUTE SHEET

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The above and other objects and benefits are achieved by providing iodine or bromine complexes of a pyrrolidonyl alkyleneoxy polymer wherein the halogen is complexed with the pyrrolidone ring as well as the alkyleneoxy group in the polymer chain. More specifically, the compounds of this invention are the halogen complexes of pyrrolidonyl alkyleneoxy polymers which possess high skin substantivity and excellent disinfectant, bactericide, sporicidal, virucidal and surfactant and coating properties.

The complexing polymers of this invention are those containing an alkyleneoxy pyrrolidonyl unit of the type:

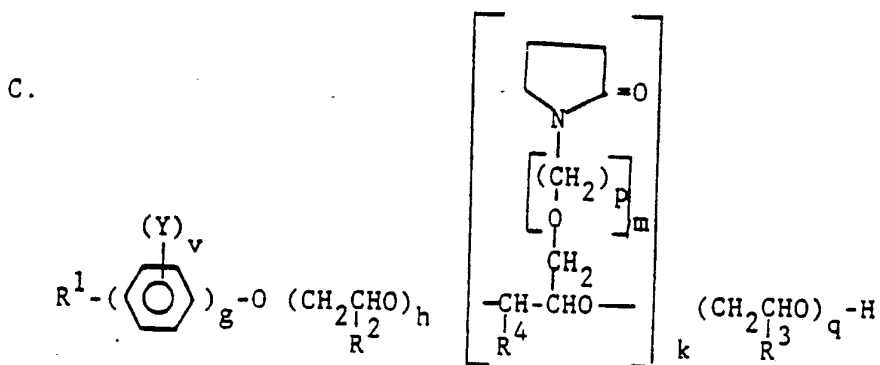


wherein R^4 is H or CH_3 ; a has a value of 1-3; m has a value of 0 or 1 and p has a value of 1 or 2, said polymers also containing at least one or more hydrophobic groups. Generally, the polymeric complexing agents contain an ethyleneoxy group, referred to herein as EO, and/or a propyleneoxy group, referred to herein as PO in the polymer chain.

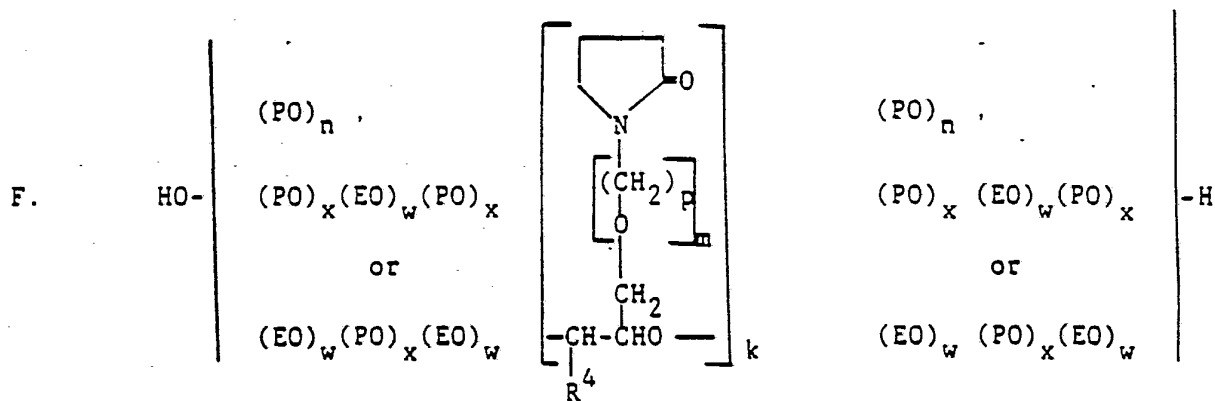
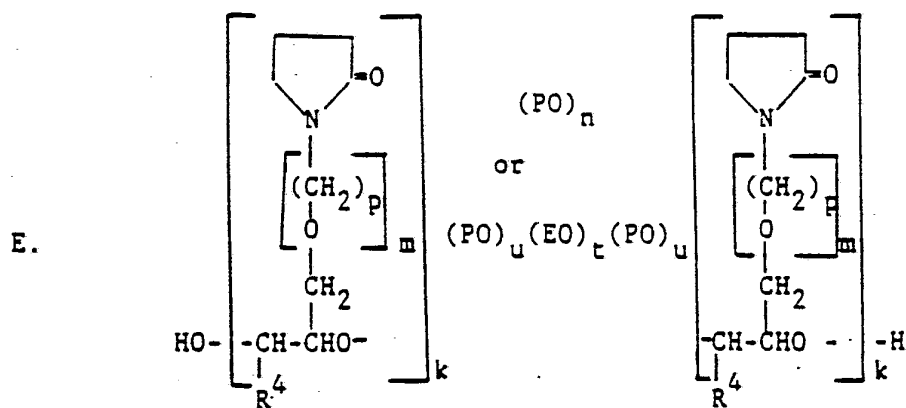
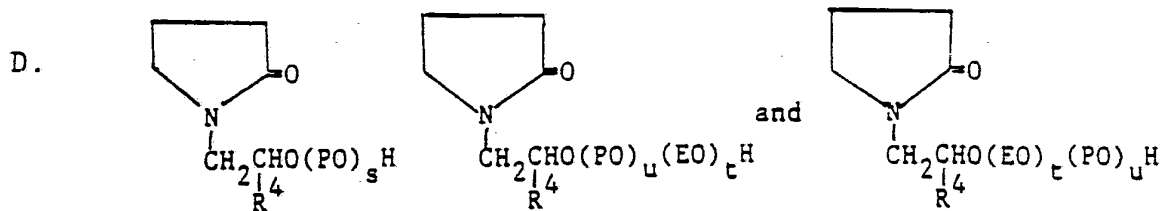
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The halogen complexes of the present invention are iodophors or bromophors and, where complexing takes place, stable complexed sites are formed. The halogen present in the complexed copolymer as available iodine or bromine can range between about 2% and about 40%, preferably between about 5% and about 25%, depending on the amount of disinfectant properties desired in the product.

Representative species of the pyrrolidonyl alkyleneoxy block copolymers with which iodine or bromine can be complexed, include the following types C-F.



wherein at least one of R^2 and R^3 , when present in the copolymer, is methyl; the remaining of groups R^2 and R^3 , when present in the copolymer, being either hydrogen or methyl; R^1 is alkyl having from 6 to 20 carbon atoms; Y is alkyl having from 1 to 4 carbon atoms; v has a value of 0 to 2; each of h and q have a value of from 0 to 100 and at least one of h and q is a positive integer, preferably an integer greater than one.



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wherein R^4 , m and p are as defined above; and g, h, k, n, q, s, t, u, v, w and x are integers having the following values

5	g = 0 or 1;	s = 2 to 200;
	h = 0 to 100;	t = 2 to 50;
	k = 2 to 200;	u = 2 to 50;
	n = 1 to 100;	v = 0 to 2;
	q = 0 to 100;	w = 1 to 25 and x = 1 to 25.

10 Since these units may occur in block or random distribution in the polymeric product, it is to be understood that their subscripts in the formulae represent the total number of designated units in the polymer and not the order of unit succession; although these units may
15 occur in block segments as indicated above.

 Preparations for the above polymers C-E are known. Specifically, the polymers of Group C where q and m are zero, and h is a positive integer are prepared by reacting an alkyleneoxylated alkylphenol with an
20 epoxyalkyl-2-pyrrolidone or, when m has a value of 1 and p has a value of 2, by reacting an alkyleneoxylated alkylphenol with the glycidol ether of N-hydroxyethyl pyrrolidone, at a temperature of between about 100°C. and about 150°C. for 0.5 to 5 hours under atmospheric
25 pressure. When m is a positive integer the polymer is prepared by reacting an aliphatic or aromatic alcohol with glycidyl ether of N-hydroxyethylpyrrolidone under the above conditions. When q is a positive integer, either of the above products are further reacted with the
30 corresponding alkylene oxide under the above conditions.

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The polymers of Group D are prepared by reacting 2-pyrrolidone with an alkylene oxide, such as propylene oxide in the presence of an alkali metal hydroxide, e.g. sodium hydroxide at a temperature between about 110°C. and about 175°C. under 15 to 50 psig. for a period of from about 0.5 to about 10 hours. When PO and EO units in the polymer are desired, the above product of Group D is further reacted with the appropriate alkylene oxide at a temperature of between about 110°C. and about 175°C. under 15 to 50 psig. for a period of from about 0.5 to about 10 hours.

The polymers of Group E are prepared by reacting polypropylene glycol with epoxypropylpyrrolidone or the glycidyl ether of N-hydroxyethylpyrrolidone at a temperature of between 100°C. and about 150°C. under from about 14 to about 50 psig. for a period of from about 0.5 to about 10 hours.

As in copending application Serial No. 020,841, now U.S. Patent No. 4,698,412, filed concurrently herewith, the polymers of Group F can be prepared by reacting a poly(N-pyrrolidonyl methyl) ethylene glycol with propylene oxide or a combination of propylene oxide and ethylene oxide under from about 14 to about 50 psig at between about 100°C. and about 150°C. for a period of from about 0.5 to about 15 hours.

Generally, any of the polymers disclosed in co-pending patent application Serial No. 021,053, entitled Epoxy Pyrrolidone Based Non-Ionic Surfactants, may be employed as a suitable polymeric moiety for complexing with iodine or bromine.

The preparation of the present complex is achieved by an economical and commercially feasible process. More particularly, iodine, bromine or a mixture of halogen and the corresponding hydrogen halide or inorganic halide salt such as the sodium or potassium salt of iodine or bromine is contacted with the pyrrolidonyl surfactant polymer. The mole ratio of halogen to hydrogen

halide or inorganic halide salt employed in the present process is between about 2:1 and about 10:1, preferably between about 3:1 and about 8:1 and the concentration of halogen based on polymer is between about 10% and about 50% by weight, preferably between about 20% and about 30% by weight. The vapor pressure of the halogen during complexing is reduced essentially to zero providing a stable complexed product.

The complexing reaction is effected at a temperature between about 20° and 85°C., preferably between 40° and about 60°C. with constant agitation under atmospheric pressure. The addition of halogen plus halide solution to polymer is accomplished in a period of from 5 minutes to 2 hours, preferably from about 20 to 45 minutes.

The complexed products of this invention can be formulated as a concentrate with disinfecting washing formulations and concentrations of the present complexes between about 0.1 and about 15 weight % of active ingredients are effective in providing an increased non-foaming cleansing action coupled with germicidal and insecticidal disinfecting properties. The optimum weight concentration of the present complexes in the concentrate formulation falls within the range of from about 0.8 to about 5 weight %.

A typical disinfectant and cleaning concentrate is represented by the formulation:

<u>Components</u>	<u>wt. %</u>
halophor complex, e.g.	
$\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2-\underset{\substack{ \\ \text{CH}_2 \\ \\ \text{N} \\ \\ \text{Cyclopentyl ring}}}{\text{CH}-\text{O}})_4-\text{H}$	8.75
phosphoric acid (75%)	8.0
iodophor base (nonionic)	5.0
water	78.25

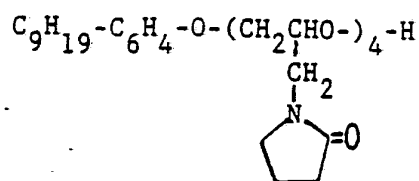
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The above formulation has 1.75% available iodine. Aliquats of 25 to 100 ppm iodine can then be made up as the disinfectant cleaning solution. The resulting solutions are lower foaming than conventional products, as demonstrated in the following examples, and are milder to the skin and stable at elevated temperatures over extended periods.

Reference is now made to the following examples which illustrate preferred embodiments but which are not to be construed as limiting to the scope of the invention as more broadly set forth above and in the appended claims.

EXAMPLE 1

Preparation of



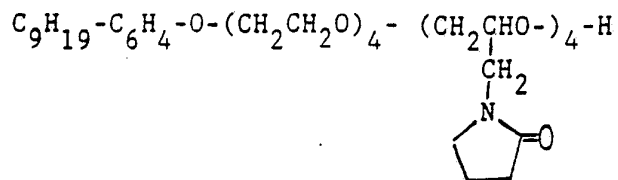
To 41.2 g. (0.2 mole) of nonylphenol in a round bottom flask was added 0.4 g. of potassium hydroxide. The mixture was heated to 120°C. under vacuum to remove water, after which 112.8 g. (0.8 mole) of N-epoxypropylpyrrolidone was added at a temperature of from 115°C. to 125°C. over a period of 1.5 hours. After addition, the resulting mixture was held at about 115°C. for an additional 3 hours. The mixture was then cooled and then neutralized with 0.4 g. of glacial acetic acid. The product had a cloud point of 70.5-71°C. (1% in water).

The iodophor of the above Example was prepared by adding 49.7 g. of iodine over a period of 30 minutes to a solution of 140 g. of nonylphenol-4 N-epoxypropyl-2-pyrrolidone adduct, in 13.3 g. of water containing 17.6 g. of sodium iodide at a temperature of 40-45°C. After the addition, the reaction mixture was held for 2 hours at 40-45°C. The resulting iodine complex was found to have 22.5% available iodine.

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EXAMPLE 2

Preparation of

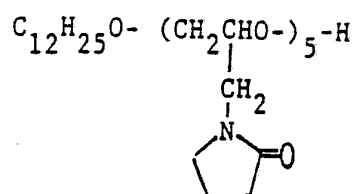


5 To 76.4 g. (0.2 mole) of nonylphenol-4 ethylene
 oxide adduct (IGEPAL CO 430) was added over a period of 2
 hours at a temperature of 115-120°C., 112.8 g. (0.8 mole)
 of 2,3-epoxypropyl-2-pyrrolidone. After the addition, the
 reaction mixture was held at 145°C. for 4 hours after
 which the product was cooled to room temperature. The
 10 product had a cloud point above 100°C. The iodophor of
 the above product was prepared by adding 49.7 g. of iodine
 over a period of 30 minutes to a solution containing 140
 g. of the epoxypropylpyrrolidone polymer obtained above in
 13.3 g. of water containing 17.6 g. of sodium iodide at a
 15 temperature of 40-45°C. After the addition, the reaction
 mixture was held for 2 hours at 40-45°C. to form the
 corresponding complexed compound.

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EXAMPLE 3

Preparation of



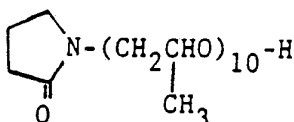
5 To 37.2 (0.2 mole) of dodecanol was added 0.4 g. potassium hydroxide and the mixture was sparged for 30 minutes at 110-115°C. with nitrogen. To this mixture was added over a 2 hour period, 141.0 g. (1.0 mole) of 2,3-epoxypyrrolidone and the resulting reaction mixture was held for an additional 3 hours at 110°-120°C. The product was then cooled and then neutralized with glacial acetic acid and was found to have a cloud point of 67-68°C. (1% in 10% NaCl).

10 The iodophor of the above compound is prepared according to the methods set forth in Example 1 employing 49.7 g. of iodine, 140 g. polymer, 13.3 g. water and 17.6 g. sodium iodide.

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EXAMPLE 4

Preparation of

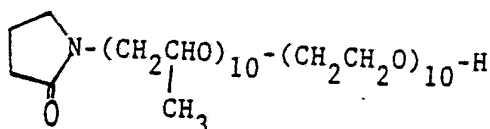


5 To a one liter autoclave was charged 85 g. (1.0
mole) of pyrrolidone and 0.5 g. of sodium hydroxide
flakes. To this mixture was added 580 g. (10 moles) of
propylene oxide over a period of 5 hours at a temperature
of 160°C. under 15-30 psig. The resulting mixture was
agitated for 30 minutes at 160°C., after which it is
10 cooled to 65°C. and a house vacuum was applied to degas
the mixture. The product (434 g.) was neutralized to a pH
of 7.4 by addition of phosphoric acid. Product analysis
by NMR indicated that 9.7 of the propylene oxide molecules
had reacted.

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EXAMPLE 5

Preparation of



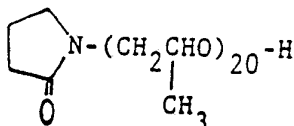
5 To a one liter autoclave was charged 266.0 g.
(0.4 mole) of the pyrrolidone-10 propylene oxide adduct
from Example 4 and 176.0 g. (4.0 moles) of ethylene oxide
was added over a period of 5 hours at 140-160°C. under a
pressure of 15 to 30 psig. The mixture was held at this
temperature for an additional 30 minutes, after which the
10 product 434 g. was cooled, discharged and neutralized with
85% phosphoric acid. By NMR analysis, it was found that
the product contained 8.4 moles of ethylene oxide. The
product was found to have a cloud point of 67°C. (1% in
water).

15 The iodophor of the above product was prepared by
adding to 139.4 g. (0.126 mole) of the above
pyrrolidone-PO-EO adduct at a temperature of 40-45°C.,
13.3 g. of water containing 17.6 g. of sodium iodide. To
this solution was added over a period of 30 minutes, 49.7
20 g. (0.39 mole) of iodine and the resulting mixture was
held for an additional 2 hours at 40-45°C. The complexed
product recovered was found to have 20.6% available iodine
and 28.7% total iodine.

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EXAMPLE 6

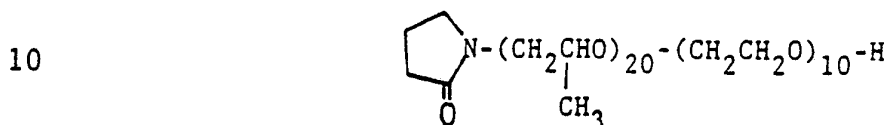
Preparation of



5 Example 4 was repeated except that 20 moles of propylene oxide is substituted therein. NMR analysis showed that 20 moles of propylene oxide had reacted. The material was found to be insoluble in water.

EXAMPLE 7

Preparation of



Using 0.4 mole of the product of Example 6, the procedure set forth in Example 5, reacting 4.0 moles of ethylene oxide is repeated. The resulting product has a cloud point of 38°C. (1% in water).

15 The iodophor of the product of this Example is prepared by adding 12 g. of water containing 13.4 g. of sodium iodide at 40°C. to 105.2 g. (0.06 mole) of the product of this Example. After the solution is clear, 37.9 g. (0.15 mole) of iodine was added over a 0.5 hour

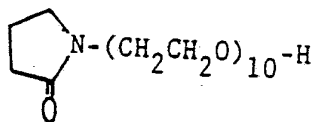
20 period. The resulting reaction mixture was held for 2 hours at 40 to 45°C. Analysis showed that the resulting iodophor product had 20.7% available iodine and 29.2% total iodine. This complexed compound was stable over 2 weeks at 50°C. and did not deposit iodine when diluted

25 with water.

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EXAMPLE 8

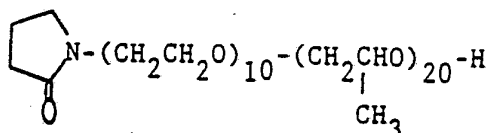
Preparation of



5 To 110.0 g. (1.29 moles) of pyrrolidone containing 0.5 g. of sodium hydroxide flakes, was gradually added 560 g. (12.9 moles) of ethylene oxide. After 5 hours, the product was cooled and analysis by NMR showed that 10.6 moles of ethylene oxide had reacted.

EXAMPLE 9

Preparation of



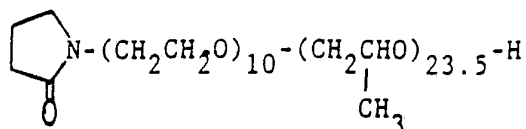
10 To 200 g. (0.38 mole) of 2-pyrrolidone-10-EO adduct obtained by Example 8 was added 440 g. (7.0 mole) of propylene oxide at a temperature of 160°C. under 30
15 psig pressure. After 5 hours the resulting product was neutralized with phosphoric acid and was found to have a cloud point of 39°C. (1 % in water). NMR analysis indicated that 18 moles of propylene oxide had reacted.

20 The iodophor of the above product is prepared by adding 20.6 g. of sodium iodide in 18.6 g. of water to 168.5 g. (0.1 mole) of the pyrrolidone-EO-PO adduct at 40-45°C. To this mixture, 56.5 g. (0.22 mole) of iodine is added and the resulting mixture stirred for 2 hours at 40-45°C. Analysis showed that the complexed product
25 contained 19.4% available iodine and 28.0% total iodine. This product was stable for 2 weeks at 50°C.

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EXAMPLE 10

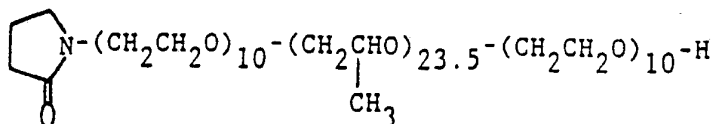
Preparation of



5 Example 9 is repeated except that 23.5 moles of propylene oxide is substituted therein. NMR analysis indicated that 23.5 moles of PO had reacted. The iodophor of this product is prepared by the procedure outlined in Example 9.

EXAMPLE 11

10 Preparation of

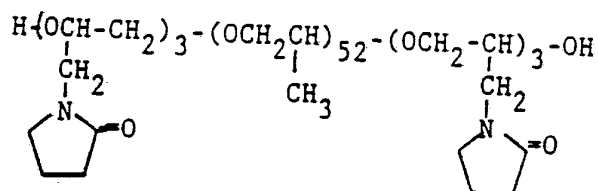


15 To the product of Example 10 is added 10 moles of ethylene oxide at a temperature of 160°C. under 30 psig. After 30 minutes the product is cooled and neutralized and analysis indicated the cloud point to be 40-43°C. (1% in water).

20 The iodophor of the above product is prepared by adding to 189 g. (0.08 mole) of the above adduct obtained in Example 11, at a temperature of 40-45°C., 29.0 g. of sodium iodide in 22.0 g. of water and 83.2 g. of iodine. The mixture is held for 2 hours at 40-45°C., after which the product is cooled to room temperature. Analysis showed that the resulting iodophor product contained 23.12% available iodine and 32.9% total iodine.

EXAMPLE 12

Preparation of

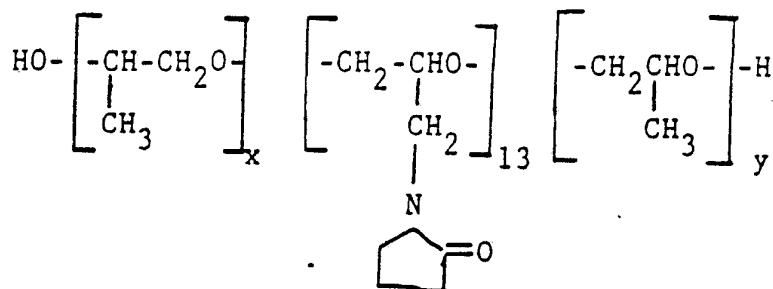


5 Into a one liter autoclave was charged 302.5 g.
(0.1 mole) of propylene glycol (molecular wt. 3025) and
0.2 grams of potassium hydroxide. The mixture was heated
to 110-115°C. and held for 1 hour with a nitrogen sparge.
Over a period of 30 minutes, 84.6 g. (0.6 mole) of
2,3-epoxypropyl-2-pyrrolidone was charged to the above
10 solution and, after the addition was completed, the
resulting mixture was held for 2 hours at 115°C. The
product was then cooled and neutralized with 0.2 g. of
glacial acetic acid. The product had a cloud point of
17.5-18°C. (1% in water).

15 The iodophor of the above adduct was made according to the method described in Example 1 except that the adduct of Example 12 is substituted therein.

EXAMPLE 13

Preparation of







wherein the sum of x and y is 30.

5 N-Epoxypropyl pyrrolidone homopolymer having a number average molecular weight of 1900 is prepared by the method of F. P. Sidelkovskaya (Vysokomol. Soedin Ser. B, 10(3), 187-189, 1968). To 1900 g or 1 mole of the homopolymer is added 0.1 wt. % of potassium hydroxide and
10 30 moles of propylene oxide at a temperature of 110-125°C. under 50 to 75 psia. After all propylene oxide is reacted or taken up (about 7 hours) the resulting copolymer is cooled neutralized with phosphoric acid, and recovered by washing with water and drying.

15 The iodophor of the copolymer product is prepared by adding about 50 g. of iodine over a period of 30 minutes to a solution of 150 g. of the copolymer product in 13.3 g. of water containing 17.6 g. of sodium iodide at a temperature of 40-45°C. The reaction mixture is then
20 allowed to stand for 3 hours at 40-45°C. after which it is cooled and recovered. The resulting iodine complex has at least 20% available iodine.

EXAMPLE 14

The extended time release and stability of the following iodophors were measured after 2 weeks at 50°C. The results of these tests are reported below.

5	Compound tested	Cloud Point 1% in H ₂ O
A	 N-(PO) ₁₀ -(EO) ₁₀ -H	67°C.
B	 N-(PO) ₂₀ -(EO) ₁₀ -H	38°C.
C	 N-(EO) ₁₀ -(PO) ₂₀ -H	39°C.
D	 N-(EO) ₁₀ -(PO) _{23.5} -(EO) ₁₀ -H	43-46°C.

10		Initial % Available Iodine	% Total Iodine	Ratio I ⁻ -I	Final* % Available Iodine
E	Iodine Complex of A	20.60	28.7	0.30	19.55
F	Iodine Complex of B	20.70	29.2	0.30	19.90
15	G Iodine Complex of C	19.45	28.0	0.30	19.45
	H Iodine Complex of D	23.12	32.96	0.35	21.93 ..

* after 2 weeks at 50°C.

EXAMPLE 15

The low foaming or foam deterrent properties of the following iodophors were tested using the standard Waring blender test. A 180 ml sample of each of the following formulations was mixed at high speed for 3 minutes. The initial foam height immediately after mixing was measured, and the foam height was remeasured after 5 minutes. The results of these tests are as follows.

	Formulation	I	II	III	IV
10	Nonionic Surfactants				
	Igepal CO-660 (1)	30.00 g			
	Compound A of Ex. 14		30.00 g		
	Compound B of Ex. 14			30.00 g	
	Compound D of Ex. 14				30.00 g
15	Iodophor				
	I-Complex of Igepal CO-660	46.00 g			
	I-Complex E in Ex. 14		46.00 g		
	I-Complex F in Ex. 14			46.00 g	
	I-Complex H in Ex. 14				46.00 g
20	75% Phosphoric Acid	83.75 g	83.75 g	83.75 g	83.75 g
	Propylene Glycol	20.00 g	20.00 g	20.00 g	20.00 g
	Distilled Water	70.25 g	70.25 g	70.25 g	70.25 g

(1) $\text{C}_9\text{H}_{19}-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{10}\text{CH}_2\text{CH}_2\text{OH}$

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Foam Test

	Formulation	Initial Foam	Foam after 5 min.
	I	17.1 mm	17.1 mm
	II	14.4 mm	0.0 mm
5	III	8.1 mm	3.6 mm
	IV	9.0 mm	5.4 mm

10 Comparison of Formulations II, III and IV containing the alkyleneoxy pyrrolidonyl iodophors with formulation I containing closely related alkyleneoxy iodophors establish the present iodophors as low foaming agents.

15 All of the above iodophor products in the foregoing Examples possess excellent surfactant and disinfectant properties. It is to be understood that any of the other polymers set forth in the disclosure can be substituted in the Examples for the preparation of their corresponding iodophors having the desirable properties of this invention. Also bromine can be substituted in the examples to provide the corresponding bromophors.

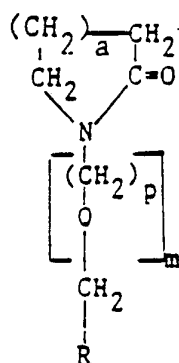
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POLYMERIC HALOPHORS

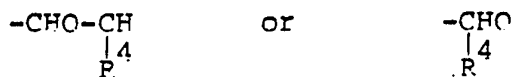
WHAT IS CLAIMED IS:

1. The halogen complex selected from the group of a iodine complex and a bromine complex of an alkyleneoxy lactam polymer containing between about 2 and about 40% halogen and said polymer contains

(i) at least one pyrrolidonyl unit having the formula



wherein a has a value of 1-3; p has a value of 1-2; m has a value of 0-1; R is a radical selected from the group of

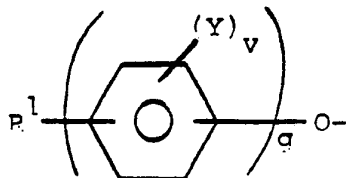


and wherein R^4 is hydrogen or methyl;

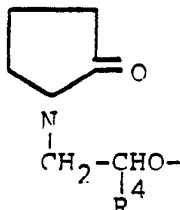
(ii) at least two propyleneoxy units and

(iii) optionally one or more ethyleneoxy units;

and said copolymer having terminal groups selected from the group consisting of hydroxy; the radical

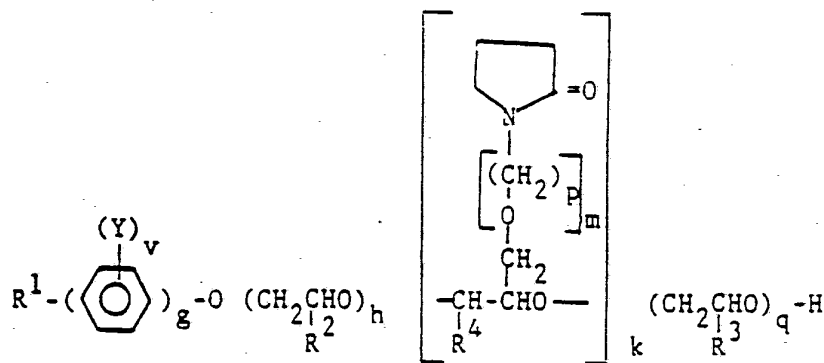


wherein R^1 is alkyl having from 6 to 20 carbon atoms; Y is alkyl having from 1 to 4 carbon atoms; v has a value of 0-2 and g has a value of 0-1; and, when m is 0 the polymer contains only one of said pyrrolidone units,



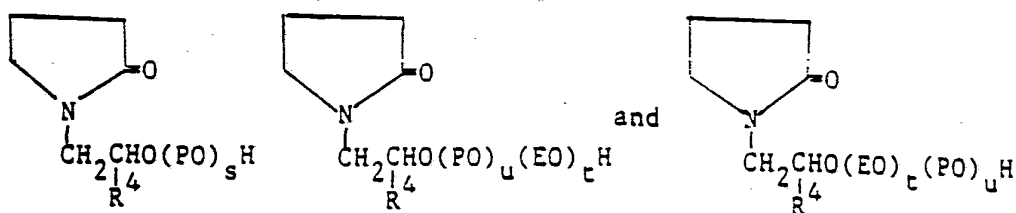
- 22 -

2. The halogen complex of Claim 1 wherein said alkyleneoxy lactam copolymer has the structure



wherein at least one of p^2 and p^3 is methyl and the remaining R^2 and R^3 is methyl or hydrogen; h has a total value of 0-100; k has a total value of 2 to 200 and q has a total value of 0-100 and at least one of h and q is a positive integer; and R^1 , R^4 , Y , q , m , p and v are as defined in Claim 1.

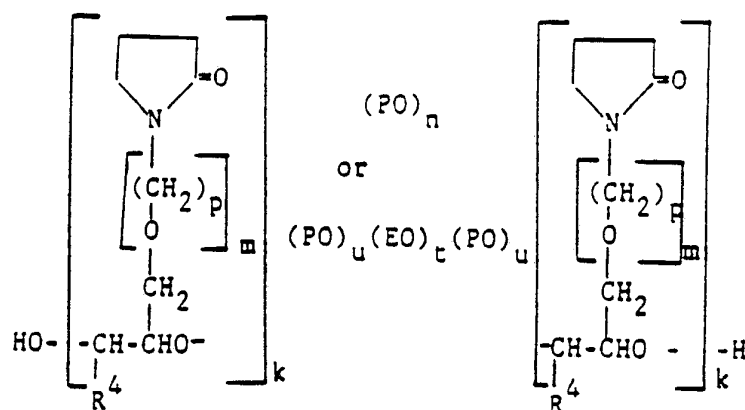
3. The halogen complex of Claim 1 wherein said alkyleneoxy lactam copolymer has the structure selected from the group of



wherein R^4 is hydrogen or methyl; s has a value of 2 to 200; t has a total value of 2 to 50 and u has a total value of 2 to 50.

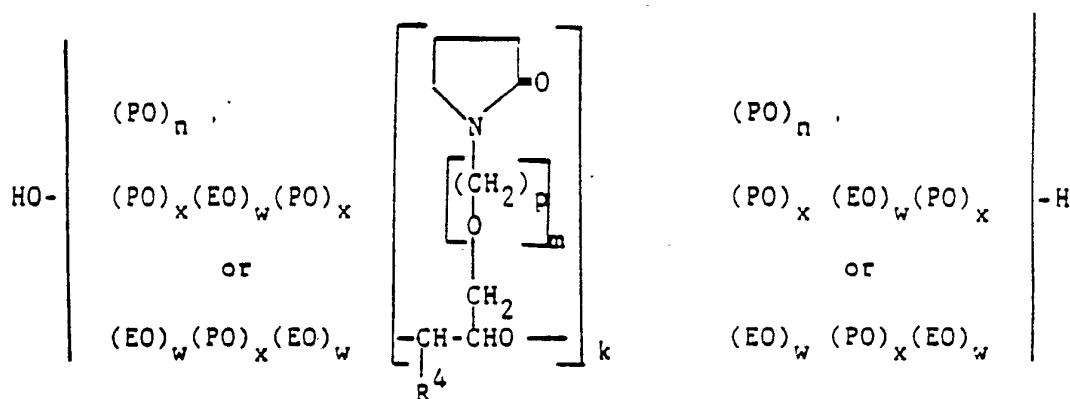
- 23 -

4. The halogen complex of Claim 1 wherein said alkyleneoxy lactam copolymer has the structure



wherein n has a total value of 1-100; t has a total value of 2-50; u has a total value of 2-50; k has a total value of 2-200.

5. The halogen complex of Claim 1 wherein said alkyleneoxy lactam copolymer has the structure



wherein k has a total value of 2-200; n has a total value of 1-100; w has a total value of 1-25 and x has a total value of 1-25.

6. The complex of Claim 2 wherein the units k and h, k and q, or k, h and q have a value greater than one and the units k and h; k and q or k and q are randomly distributed in the copolymer.

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7. The complex of Claim 3 containing units u and t and wherein the units u and t are randomly distributed in the copolymer.

8. The complex of Claim 4 wherein the copolymer contains units k and n, and wherein n has a value greater than one and the units k and n are randomly distributed in the copolymer.

9. The complex of Claim 4 wherein the copolymer contains units k, u and t and wherein the units k, u and t are randomly distributed in the copolymer.

10. The complex of Claim 5 wherein the alkyleneoxy unit is $(PO)_n$ and wherein the unit n has a value greater than one and k and n are randomly distributed in the copolymer.

11. The complex of Claim 5 wherein the alkyleneoxy units are $(PO)_u$ and $(EO)_t$ and wherein the units k, x and w are randomly distributed in the copolymer.

12. The complex of Claim 2 wherein the units k and h, k and q or k, h and q have a value greater than one and wherein each the units k and h, k and q or k, h and q form blocks in the copolymer chain.

13. The complex of Claim 3 wherein the copolymer contains units u and t and wherein each of the units u and t form blocks in the copolymer chain.

- 25 -

14. The complex of Claim 4 wherein the copolymer contains units k and n and n has a value greater than one and each of the units k and n form blocks in the polymer chain.

15. The complex of Claim 4 wherein the copolymer contains units k, u and t and wherein each of the units k, u and t form blocks in the polymer chain.

16. The complex of Claim 5 wherein the alkyleneoxy unit is $(PO)_n$, n has a value greater than one and each of the units k and n form blocks in the polymer chain.

17. The complex of Claim 5 wherein the alkyleneoxy units are $(PO)_u$ and $(EO)_t$ and wherein each of the units k, u and t form blocks in the polymer chain.

18. The process of adding an effective cleansing and disinfecting amount of the complex of Claim 1 to a detergent solution.

19. The process of Claim 18 wherein the complex of Claim 1 is an iodophor and between about 0.1 and about 15 weight % of the iodophor based on active ingredients is added to the detergent solution.

20. The process of adding an effective disinfecting amount of the complex of Claim 1 to topical medicinal solution for extended and gradual release of halogen.

21. The process of Claim 20 wherein the complex of Claim 1 is an iodophor and between about 0.1 and about 15 weight % of the iodophor based on active ingredients is added to the medicinal solution.

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22. The process of adding an effective cleansing and disinfecting amount of the complex of Claim 2 to a detergent solution.

23. The process of adding an effective cleansing and disinfecting amount of the complex of Claim 3 to a detergent solution.

24. The process of adding an effective cleansing and disinfecting amount of the complex of Claim 4 to a detergent solution.

25. The process of adding an effective cleansing and disinfecting amount of the complex of Claim 5 to a detergent solution.

26. The process of adding an effective disinfecting amount of the complex of Claim 2 to topical medicinal solution for extended and gradual release of halogen.

27. The process of adding an effective disinfecting amount of the complex of Claim 3 to topical medicinal solution for extended and gradual release of halogen.

28. The process of adding an effective disinfecting amount of the complex of Claim 4 to topical medicinal solution for extended and gradual release of halogen.

29. The process of adding an effective disinfecting amount of the complex of Claim 5 to topical medicinal solution for extended and gradual release of halogen.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US88/00415**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (4) A01N 43/06; C07D 207/00; C08G 69/24; C11D 3/48 US, CL: 525/240; 528/523, 326; 548/519, 551																							
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; padding: 5px;">Classification System</th> <th style="border: 1px solid black; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: middle; padding: 10px;">U.S.</td> <td style="border: 1px solid black; padding: 10px;">525/240; 528/323, 323, 326; 548/519, 551; 514/424; 252/106; 424/150</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	525/240; 528/323, 323, 326; 548/519, 551; 514/424; 252/106; 424/150																	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 5px;">Category [*]</th> <th style="width: 60%; border: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,017,407 (CANTOR) 12 APRIL 1977, SEE COLUMN 2, LINES 11-68.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,113,857 (SHETTY) 12 SEPTEMBER 1978, SEE COLUMN 2, LINES 58-68.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,408,001 (GINTER) 04 OCTOBER 1983, SEE COLUMN 1, LINES 14-31.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,481,167 (GINTER) 06 NOVEMBER 1984, SEE COLUMN 1, LINES 22-39.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">GB, A, 2,139,088 (VAN PASSEN) 07 NOVEMBER 1984, SEE PAGE 1, LINES 24-52.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y,P</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,698,412 (TRACY) 06 OCTOBER 1987, SEE COLUMN 1 AND COLUMN 2 AND CLAIMS 1-4.</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	US, A, 4,017,407 (CANTOR) 12 APRIL 1977, SEE COLUMN 2, LINES 11-68.	1-17	Y	US, A, 4,113,857 (SHETTY) 12 SEPTEMBER 1978, SEE COLUMN 2, LINES 58-68.	1-17	A	US, A, 4,408,001 (GINTER) 04 OCTOBER 1983, SEE COLUMN 1, LINES 14-31.	1-17	A	US, A, 4,481,167 (GINTER) 06 NOVEMBER 1984, SEE COLUMN 1, LINES 22-39.	1-17	Y	GB, A, 2,139,088 (VAN PASSEN) 07 NOVEMBER 1984, SEE PAGE 1, LINES 24-52.	1-17	Y,P	US, A, 4,698,412 (TRACY) 06 OCTOBER 1987, SEE COLUMN 1 AND COLUMN 2 AND CLAIMS 1-4.	1-17
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>																							
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 10px;">02 MAY 1988</td> <td style="border: 1px solid black; text-align: center; padding: 10px;">13 JUN 1988</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 10px;">ISA/US</td> <td style="border: 1px solid black; text-align: center; padding: 10px;"> ALLAN LIEBERMAN </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	02 MAY 1988	13 JUN 1988	International Searching Authority	Signature of Authorized Officer	ISA/US	 ALLAN LIEBERMAN													
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International Searching Authority	Signature of Authorized Officer																						
ISA/US	 ALLAN LIEBERMAN																						

PCT/US88/00415

PCT/ISA210 VI. CONT.

III. CLAIMS 20, 21 AND 26-29: THE PROCESS OF ADDING
THE COMPLEX TO A MEDICINE: CLASS 514, SUBCLASS 424.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

I. CLAIMS 1-17, DRAWN A HALOGEN COMPLEX OF A POLYMER: CLASS 525, SUBCLASS 420.

II. CLAIMS 18, 19 AND 22-25, DRAWN TO PROCESS OF ADDING THE COMPLEX OF GROUP I TO A DETERGENT: CLASS 252, SUBCLASS 106.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

1-17

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.